



Inventors: Boris Bronfin et al.

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1

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For: CREEP RESISTANT MAGNESIUM ALLOYS

WITH IMPROVED CASTABILITY

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Sir:

DECLARATION OF PROF. BORIS BRONFIN

I hereby declare as follows:

1. I received Ph.D. and D.Sc. degrees from the Urals Polytechnic University in 1974 and 1988, respectively. Since that time I have been active in the field of physical metallurgy, particularly in the field of magnesium alloys. Based on numerous citations of my publications around the world, I was included in MARQUIS Who's Who in Science and Engineering, 2005-2006 (8<sup>th</sup> Edition), which distinguishes

scientists who are leading achievers in certain fields of Science and Engineering.

2. I have been employed by Dead Sea Magnesium Ltd since 1992. My current position is a head of Physical Metallurgy and Processing Department. The experiments included in this declaration were carried out under my direct supervision.
3. I am one of the co-inventors and co-applicants of the above identified application and I am familiar with the prosecution of this case. I have reviewed the following patent documents:
  - US 2001/0023720 to Ohori et al. (denoted US/20 hereinafter);
  - US 6,139,651 to Bronfin et al. (denoted US/51 hereinafter);
  - US 6,342,180 to Lefebvre et al. (denoted US/80 hereinafter);
  - EP 1127950 (denoted EP/50 hereinafter); and
  - JP 06200348 (denoted JP/48 hereinafter).
4. The cited documents, like the instant application, deal with magnesium alloys, but they do not provide alloys with castability and creep resistance of our invention, as is shown below (par. 6-10).

Light magnesium alloys have naturally many applications, and every application has different requirements on their physical and mechanical properties (ductility, strength, creep resistance, corrosion performance, fluidity in molten state, casting properties, thermal conductivity, etc.). Since most elements of the Periodic Mendeleev Table are used in Mg alloys (see, e.g., Annex 1 – Avedesian, Table 4), finding a suitable composition, among so many combinations, with a required behavior for a given application is a matter of extensive experimentation. The number of factors affecting said behavior, nearly

as high as the number of said element combinations, includes, e.g., the formation of intermetallic compounds whose presence radically changes the alloy properties. The formation of intermetallic compounds, as well as other factors, is affected in a very sensitive way by the presence of minor alloying elements, leading to a hardly predictable, nonlinear effects on behavior.

A complex phase diagram of a simple mixture, containing only two components, nicely illustrates the complexity of the problems in this field (Annex 2 – Ullmann, Figure 1), especially when bearing in mind that usually more than seven elements are present in an Mg alloy. These situations illustrate a multi-parameter problem; a combination of elements leading to certain properties cannot be relied upon to foresee the properties of another combination, even when the two combinations seem similar, because the extrapolation and prediction are not trivial, and sometimes are impossible to make. In practical situations, another factor adds to the above complexity – high costs of some of the used elements.

5. Our invention provides alloys with a low creep rate for such applications in which good castability is a predominant requirement. Castability is characterized by the instant inventors by a combination of three parameters that are important for the intended usage (Table 3 of the application), namely for the usage in automotive and aerospace systems (Par. [0034] of the instant application publication). The alloys are ranked by an integrated score.

Tables 3 and 4 of the application demonstrate the superiority of the alloys according to the invention over comparative alloys including commercial materials. The castability of all alloys according to the

invention is better than the castability of the comparative alloys, except for Comparative Example 1. The commercial alloy of Comparative Example 1, although having good castability, is not usable for the intended application, due to its inferior creep properties (see Table 4), which again demonstrates the abovementioned difficulty of selecting an optimal element combination, in this multi-parametric system, ensuring that more than one desired parameter would have acceptable values. That was the challenge in developing the alloys of this application: to provide alloys having good castability without compromising creep rate, and possibly, but not necessarily, strength and corrosion resistance.

6. Document US/20 claims die casting alloys with Al content 2 to 6 wt %, preferably not exceeding 5 wt% (see Tables 1 and 2 of the document). Our application discloses alloys with Al content from 6.1 wt% to 9.2 wt%. Additional results, not included in the specification, for two alloys prepared according to the cited document, US/20, enabling a direct comparison of alloys according to the two documents, are presented in Tables 1A, 3A, and 4A (Annex 4), which are original Tables 1, 3, and 4 to which results for two additional Comparative Examples 6 and 7 have been added.

Here, I would like to note that during the R&D related to our alloys, we set the following values of castability and creep rate as acceptability limits for our new alloys: castability rank at least 85 and creep rate (150°C, 50 MPa) not higher than 4. However, for practical industrial applications alloys having castability of at least 95 are employed. As the enclosed tables show, all examples according to the invention fall into the acceptability limits, whereas all comparative examples are outside those limits, Comparative Example 1 leading to an alloy which

is unsuitable because of its creep rate, and all the others because of their castability.

I wish to emphasize that all alloys falling into the ambit of the instant application are in the above-defined acceptability limits, even if they have an Al content lower than 6.1 wt% (Examples 1, 2, and 4), whereas the alloys according to US/20 are outside the limits and do not comply with the above-defined requirements (Examples 6 and 7).

It may be noted that Examples 6 and 7 of Annex 5 have the same compositions as typical compositions in Table 1 of US/20, whereas Examples 1, 2, and 4 of the instant application are outside the ambit of US/20, since they differ, e.g., by their Ca content from the allowed range of US/20.

7. US/51, of which I am a co-inventor, provides alloys with relatively lower Sr content, exemplified by 0.12 or less wt%, and relatively higher Be content, exemplified by 7-11 ppm (Table 1 of US/51), whereas the instant application employs higher Sr contents with Be not exceeding 4 ppm (instant Table 1). These are substantially distinct alloys from physical metallurgy point of view
  
8. US/80 broadly claims nearly all practical combinations of elements, since the document practically restricts the alloys merely by one element range in claim 1, namely by Al content, all other elements being optional. In addition, said one element is claimed in the whole practically used range (Annexes 2 and 3), namely from 1 to 12 wt%. However, the cited document practically demonstrates only one alloy, an alloy that has a narrow range of elements, approximately as follows:  $5.2 \pm 0.1$  wt% of Al;  $0.4 \pm 0.1$  wt% of Sr;  $0.2 \pm 0.1$  wt% of Ca; and 0.3 wt% of

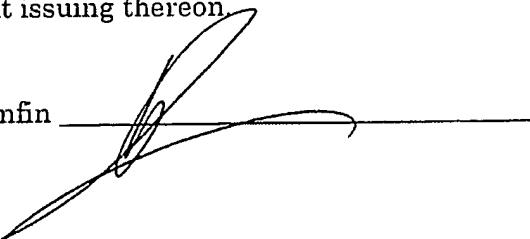
Mn (Table 1 of the document). To me, as a scientist, such a disclosure, without suitable examples, is meaningless, because of the extreme component effect described in paragraph 4 above.

9. EP/50 and US/20 are nearly identical; therefore, all my comments regarding US/20 in the paragraph 6 are applicable also to EP/50.
10. Regarding JP/48, I should note that some of the alloys that are in the ambit of this document simply cannot be made, as evident on the basis of Metallurgic Science. For example, it is known that aluminum is not compatible with zirconium (Annex 3 – Emley, and Annexes 1 and 2). Zirconium forms stable compounds with certain elements, aluminum being one of them, and thus is removed from solid solution. Consequently, the metallic mixtures according to JP/48, comprising Zr cannot be formulated into alloys. However, the document does not teach which of the claimed mixtures could be used as alloys and which only as a multiphase, heterogeneous mixtures (see, e.g., Annex 3, page 127, line 1; Annex 1, page 15, paragraph about Zr, Annex 2, page 585, paragraph 2.2).

I hereby declare that all statements made herein of my own knowledge are true and that all statements made herein on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the subject application or any patent issuing thereon.

Dated: 20/12/09

Boris Bronfin

A handwritten signature in black ink, appearing to read "Boris Bronfin", is written over a horizontal line. The signature is fluid and cursive, with a large, stylized 'B' at the beginning.

# *ANNEX 1*

## **ASM Specialty Handbook®**

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### **Magnesium and Magnesium Alloys**

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and  
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ASM International (Retired)

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Comments, criticisms, and suggestions are invited, and should be forwarded to ASM International.

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Table 4 Liquid solubility and alloying efficiency of alloying additions to magnesium

Added element	Form of addition	Apparent liquid solubility, %	Alloying efficiency, %
Aluminum	Metal	100	90-100
Antimony	Metal	100	100
Arsenic	Metal granules		60-100
Barium	Metal	100	25-100
Beryllium	Al-Be BeCl <sub>2</sub>	0.01	10-30
Bismuth	Metal	100	100
Boron	BCl <sub>3</sub>		<5
Cadmium	Metal Powder		
Calcium	Metal 80Cs-20Mg	100	50-100
Cesium	Metal sealed in glass ampule		0 (contained 0.23 Si)
Chromium	Metal Metal powder CrCl <sub>3</sub>	0.04	0-8
Cobalt	Metal powder Metal turnings	-5	1-100
Copper	Metal	100	100
Gallium	Metal shot	100	85-100
Germanium	Metal	100	70-100
Gold	Metal	100	100
Indium	Metal	100	95-100
Iodine	I <sub>2</sub>		0
Iron	Metal powder Metal turnings	-0.1	10
Lead	FeCl <sub>3</sub>		
Lithium	Metal	100	100
Manganese	MnCl <sub>2</sub> as #250 flux Al-Mn Mn powder Mn platelets	-5.0	95
Mercury	Metal	100	50-90
Mischmetal (RE metals)	Metal REF <sub>3</sub> and RECl <sub>3</sub>	100	50-90
Molybdenum	MoCl <sub>4</sub>	≥10	80-100
Nickel	Metal powder Metal	100	100
Niobium	Metal	0	0
Osmium	Metal powder		58
Palladium	Metal	100	100
Phosphorus	Fe <sub>2</sub> P	-0.01	0-60
Platinum	Metal	100	100
Potassium	Metal	-0.02	5-15
Rhodium	Metal	-0.5	100
Rubidium	Metal sealed in glass ampule	0	0 (contained 0.10 Si)
Ruthenium	Metal powder	≥0.003	<1
Samarium	Mixture of RE metals	0	0
Selenium	FeSi (95% Si)	100	0-38
Silicon	Metal powder		35-85
Silver	Metal	100	100
Sodium	Metal	-0.1	10-80
Strontium	Metal	100	30-100
Tantalum	Metal	-0.015	0
Tellurium	Metal powder		0-1.5
Thallium	Metal	-0.2	20-50
Thorium	Metal	100	95-100
Tin	ThF <sub>4</sub> and ThCl <sub>4</sub>	100	75-100
Titanium	Metal	≥10	0-100
Tungsten	TiCl <sub>4</sub>	≥0.2	10
Uranium	Metal powder	..	<10
Vanadium	VCl <sub>4</sub>	≥0.02	0
Yttrium	REF <sub>3</sub> mix		-10
Zinc	Metal	100	95-100
Zirconium	Metal	0.95	20-50

## Effects of Alloying Constituents

The physical properties of magnesium are, of course, affected by the amount of each alloying constituent added to it. In many instances, the effect is more or less directly proportional to the amount added, up to the limits of solid solubility at the temperature at which the property is measured (see Fig. 3). The processing and property effects of the individual alloying elements, however, are more important in most structural applications than the physical properties. Descriptions of these effects follow for the elements commonly used in commercial magnesium alloys.

Aluminum has the most favorable effect on magnesium of any of the alloying elements. It improves strength and hardness, and it widens the freezing range and makes the alloy easier to cast. When present in amounts in excess of 6 wt%, the alloy becomes heat treatable, but commercial alloys rarely exceed 10 wt% aluminum. An aluminum content of 6% yields the optimum combination of strength and ductility.

Beryllium. Although only slightly soluble in magnesium, adding up to about 0.001 wt% beryllium decreases the tendency for the surface of the molten metal to oxidize during melting, casting, and welding. It can be used successfully in die-cast and wrought alloys, but must be used judiciously in sand-casting alloys because of its grain-coarsening effect.

Calcium is a special alloying ingredient added in very small amounts by some manufacturers to assist in metallurgical control. It serves a dual purpose: when added to casting alloys immediately prior to pouring, it reduces oxidation in the molten condition as well as during subsequent heat treatment of the casting, and it improves the rollability of magnesium sheet. The addition of calcium must be controlled to below about 0.3 wt%, however, or the sheet will be susceptible to cracking during welding.

Copper adversely affects the corrosion resistance of magnesium alloys if present in quanti-

Table 5 Interfacing elements in molten magnesium

Al-Ba	Fe-Li
Al-Co	Fe-Zr
Al-Fe(a)	Li-MM-Mn
Al-Mn(a)	Li-Mn
Al-MM-Li	Li-Ni
Al-Ni	Li-Sb
Al-Th	Li-Th
Al-Zr ✓	Li-Zr
B-Fe	MM-Sb
B-Mn	MM-Si
Be-Fe	Mn-Si
Be-Mn	Mn-Zr ✓
Be-Zr	Ni-Zr
Bi-Ca	Pb-Zr
Bi-Li	Sb-Th
Ca-Sb	Sb-Zr
Co-Zr	Si-Th
Cu-Li	Si-Zr

Note: Other compounds have been reported that, when each element is considered individually, would be expected to be soluble in molten Mg. Some of these high-melting compounds probably would not be soluble in molten Mg. (a) Probably a ternary combination.

ties exceeding 0.05 wt% However, it improves high-temperature strength.

**Iron** is one of the more harmful impurities in magnesium alloys in that it greatly reduces the corrosion resistance if present in even small amounts. In ordinary commercial-grade alloys, the iron content can average as high as 0.01 to 0.03 wt%. For maximum resistance to corrosion, however, 0.005% is specified as the upper limit for iron content.

Lithium has relatively high solid solubility in magnesium (5.5 wt%, 17.0 at%), and because of its low relative density of 0.54, it has attracted interest as an alloying element in magnesium alloys to lower the density to values even lower than that of unalloyed magnesium. Moreover, only some 11 wt% of lithium is needed to form the  $\beta$  phase, which has a body-centered cubic (bcc) crystal structure (rather than a hexagonal close-packed, or hcp, structure), thereby improving formability of wrought products. The addition of lithium decreases strength, but increases ductility. Mg-Li alloys are also amenable to age hardening, although they tend to overage at only slightly elevated temperatures (e.g., 60 °C. or 140 °F). So far, Mg-Li alloys have found only limited application.

Manganese does not have much effect on tensile strength, but it does increase yield strength slightly. Its most important function is to improve the saltwater resistance of Mg-Al and Mg-Al-Zn alloys by removing iron and other heavy-metal elements into relatively harmless intermetallic compounds, some of which separate out during melting. The amount of manganese that can be added is limited by its relatively low solubility in magnesium. Commercial alloys containing manganese rarely contain over 1.5 wt%, and in the presence of aluminum, the solid

solubility of manganese is reduced to about 0.3 wt%.

Nickel is like iron in that it is another of the more harmful impurities in magnesium alloys because it also greatly reduces the corrosion resistance if present in even small amounts. In ordinary commercial-grade alloys, the nickel content can average as high as 0.01 to 0.03 wt%, but for maximum resistance to corrosion, 0.005% is specified as the upper limit for nickel content.

Rare earth metals are added to magnesium alloys either as mischmetal or as didymium. Mischmetal is a natural mixture of the rare earths containing about 50 wt% cerium, the remainder being principally lanthanum and neodymium; didymium is a natural mixture of approximately 35% neodymium and 15% praseodymium.

Additions of the rare earths increase the strength of magnesium alloys at elevated temperatures. They also reduce weld cracking and porosity in casting because they narrow the freezing range of the alloys.

**Silicon.** The addition of silicon to magnesium alloys has been found to increase fluidity of the metal in the molten state. However, it decreases corrosion resistance of magnesium alloys if iron is also present in the alloy.

Silver additions improve the mechanical properties of magnesium alloys by increasing response to age hardening.

Thorium additions increase the creep strength of magnesium alloys at temperatures up to 370 °C (700 °F). The most common alloys contain 2 to 3 wt% thorium in combination with zinc, zirconium, or manganese. Thorium improves the weldability of alloys containing zinc.

Tin is useful when alloyed with magnesium in combination with small amounts of aluminum. The tin serves to increase the ductility of the

alloy and makes it better for hammer forging because it reduces the tendency for the alloy to crack while being hot worked.

Zinc is next to aluminum in effectiveness as an alloying ingredient in magnesium. Zinc is often used in combination with aluminum to produce improvement in room-temperature strength; however, it increases hot shortness when added in amounts greater than 1 wt% in magnesium alloys containing 7 to 10 wt% aluminum. Zinc is also used in combination with zirconium, rare earths, or thorium to produce precipitation-hardenable magnesium alloys having good strength. Zinc also helps overcome the harmful corrosive effect of iron and nickel impurities that might be present in the magnesium alloy.

Zirconium has a powerful grain-refining effect on magnesium alloys. It is thought that because the lattice parameters of  $\alpha$ -zirconium ( $a = 0.323$  nm,  $c = 0.514$  nm) are very close to those of magnesium ( $a = 0.320$  nm,  $c = 0.520$  nm), zirconium-rich solid particles produced early in the freezing of the melt may provide sites for the heterogeneous nucleation of magnesium grains during solidification.

Zirconium is added to alloys containing zinc, rare earths, thorium, or a combination of these elements where it serves as a grain refiner (up to its limit of solid solubility). However, it cannot be used in alloys containing aluminum or manganese because it forms stable compounds with these elements and is thus removed from solid solution. It also forms stable compounds with any iron, silicon, carbon, nitrogen, oxygen, and (mainly) hydrogen present in the melt. Because only the portion of the zirconium content available for grain refining is that which is in solid solution, the soluble zirconium content, rather than the total zirconium content, is the value important to the alloy.

Yttrium has a relatively high solid solubility in magnesium (12.4 wt%) and is added with other rare earth elements to promote creep resistance at temperatures up to 300 °C (570 °F). About 4 to 5% Y is added to magnesium to form commercial alloys such as WE54 and WE43, where it imparts good elevated-temperature properties up to about 250 °C (480 °F).

### Commercial Alloy Systems

The five basic groups of alloy systems that are currently being commercially produced are based on the major alloying elements: manganese, aluminum, zinc, zirconium, and rare earths. These are subdivided as follows:

- Magnesium-manganese
- Magnesium-aluminum-manganese
- Magnesium-aluminum-zinc-manganese
- Magnesium-zirconium
- Magnesium-zinc-zirconium
- Magnesium-rare earth metal-zirconium
- Magnesium-silver-rare earth metal-zirconium
- Magnesium-yttrium-rare earth metal-zirconium

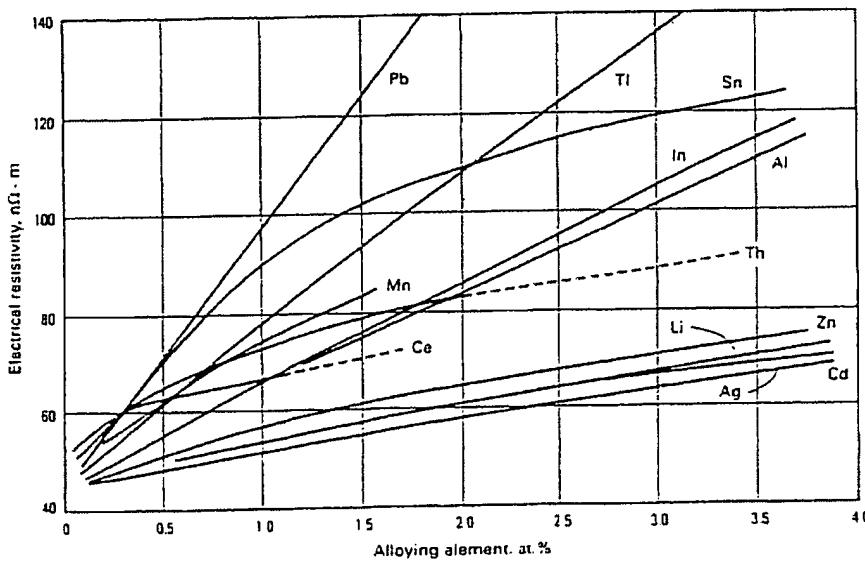


Fig. 3 Effect of alloying additions on the electrical resistivity of magnesium. Source: Ref 12, 13

## *ANNEX 2*

This is a reprint of an article from the fifth edition of

# **Ullmann's Encyclopedia of Industrial Chemistry**

Ullmann's has a long and successful tradition. The first compilation of its kind appeared in 1914 and its fourth edition was completed in 1984.

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lanthanum, lithium, manganese, neodymium, silver, thorium, yttrium, zinc, and zirconium.

### 2.1. Magnesium-Aluminum Alloys

Aluminum is by far the most important alloying element for magnesium. Its maximum solid solubility in the Mg-Al system is 12.7 wt% at the eutectic temperature 437°C (Fig. 1). The eutectic contains 32 wt% aluminum, and its composition is  $Mg_{17}Al_{12}$ . Commercial alloys contain less than 10 wt% aluminum and, according to the equilibrium diagram, should solidify into a homogeneous matrix of magnesium with aluminum in solid solution. This is, however, not the case—a relatively large volume fraction of eutectic constituents is formed (Fig. 2). The solidification diagram shows a distinct plateau at the eutectic temperature (Fig. 3).

Scheil's equation describes freezing under nonequilibrium conditions where solute diffusion is negligible, resulting in a strongly segregated material. The fraction solidified as a function of temperature for equilibrium and nonequilibrium freezing is illustrated in Figure 4 for two Mg-Al alloys. In practice, the Scheil equation provides a reasonable description of solidification during commercial casting processes.

The Mg-Al equilibrium diagram is typical of an age-hardenable system. After solution heat treatment at temperatures just below the eutectic temperature, the  $\beta$ - $Mg_{17}Al_{12}$  phase dissolves, and subsequent quenching gives a supersaturated solid solution. During artificial aging at 150–220°C, a platelike precipitate forms, resulting in a significant hardening effect. A certain quench

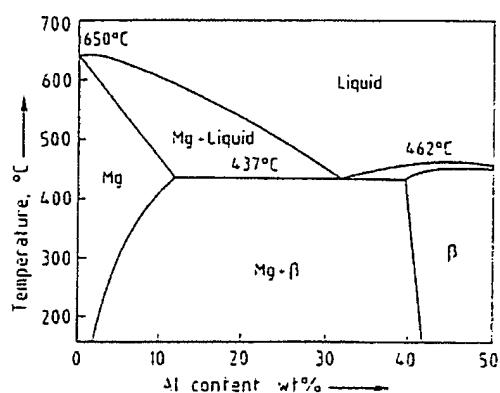


Figure 1. Phase diagram for the binary system Mg-Al



Figure 2. Microstructure of low-pressure die-cast AM100 alloy ( $\times 200$ )

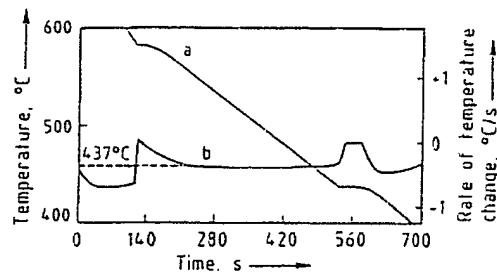


Figure 3. Solidification diagram showing the temperature variation during cooling of the Mg-Al alloy AM 100 A  
a) Temperature; b) Rate of temperature change

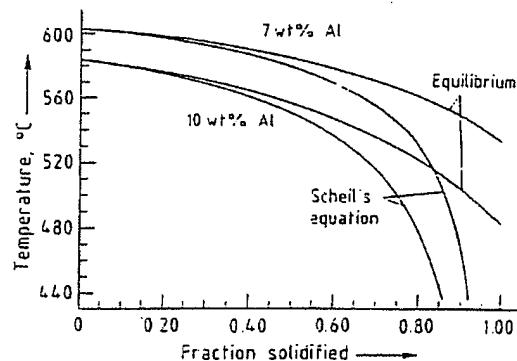


Figure 4. Fraction solidified as a function of temperature calculated for equilibrium and nonequilibrium conditions for two Mg-Al alloys

sensitivity is caused by a competing reaction, whereby the  $\beta$ -phase precipitates discontinuously along grain boundaries. This process occurs during cooling after casting or following solution heat treatment.

Commercial Mg-Al alloys usually contain a small amount of zinc (0–2 wt%), which strengthens them somewhat. Higher zinc levels increase the amount of eutectic constituents, lower the solidification temperature, and may cause hot shortness (cracking). Solution treatment of Mg-Al-Zn alloys increases their ductility. In the absence of solution heat treatment (as with high-pressure die-cast products), maximum ductility is obtained by using alloys of low aluminum and zinc content (e.g., AM60 alloy containing 6 wt% aluminum). Further improvement of ductility is possible with even less aluminum, but castability suffers somewhat.

High-temperature applications require improved creep properties, which are achieved by decreasing the aluminum content and thus the volume fraction of the low melting point eutectic. Further improvements are possible by introducing elements that form finely dispersed particles in the matrix (dispersion hardening). In high-pressure die-cast parts that solidify rapidly, silicon addition causes the formation of finely dispersed MgSi particles; this is the basis of Mg-Al-Si alloys.

Manganese addition plays a crucial role in controlling the iron level by reducing the solubility of iron in the melt. Several high-purity alloys with greatly improved corrosion resistance are now available commercially. Grain refining, when necessary, is performed by introducing carbon into the melt at > 750 °C (preferably ca. 780 °C).

## 2.2. Grain-Refined Magnesium-Zirconium Alloys

A series of high-performance magnesium-base alloys was developed after discovery of the extremely efficient grain-refining action of zirconium. This effect results from formation of a high density of tiny zirconium particles in the melt, which act as potent grain nuclei. An example of a zirconium-refined grain structure is shown in Figure 5. Unfortunately, elements such as aluminum and manganese lower the solubility of zirconium in the melt, thus precluding exploitation of this grain-refining mechanism in common aluminum-containing alloys.

**Mg-Zn-RE-Zr.** Binary Mg-Zn alloys show inferior mechanical properties and cast-

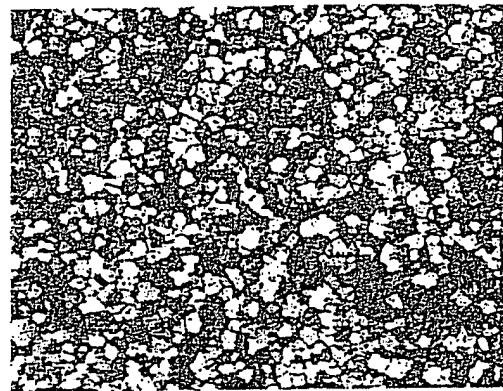


Figure 5. Structure of a zirconium grain-refined alloy RZ5 (x 50)

bility, but the addition of zirconium for grain refinement and rare earth (RE) elements to reduce microporosity, led to the development of alloys such as EZ33 and ZE41. These alloys have been used widely as sand castings in the T5 condition (cooled and artificially aged) for applications involving exposure to moderately elevated temperature (up to ca. 200 °C). The ZE63 alloy is a high-strength variant in which solution heat treatment in a hydrogen atmosphere is employed to remove some of the embrittling Mg-Zn-RE grain boundary phases. In extrusion, microporosity is of less concern and Mg-Zn-Zr alloys are used without RE additions.

**Mg-Ag-RE-Zr.** Addition of silver and neodymium-rich misch metal, in addition to zirconium, promotes age hardening efficiently when the alloy is given a full T6 treatment (solution heat-treated and artificially aged). The precipitates formed are relatively stable; the alloy shows high mechanical strength and good creep properties at temperatures approaching 250 °C.

**Mg-Y-RE-Zr.** The most recently developed alloy system for high-temperature application is based upon additions of yttrium and neodymium-rich misch metal. This alloy system was developed to meet the ever-increasing high-temperature performance requirements of the aerospace industry and may replace the Mg-Ag-RE-Zr and thorium-containing alloys. The alloys must be melted in a special inert atmosphere (argon) and develop their properties by T6 heat treatment.

# **ANNEX 3**

## **PRINCIPLES OF**

# **Magnesium Technology**

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## CHAPTER V

# ALLOYING AND REFINING OF ALLOYS CONTAINING ZIRCONIUM

### INTRODUCTION

The remarkable development since World War II of the family of magnesium-zirconium alloys is based on the discovery by F. Sauerwald in 1947 of the exceptional grain-refining action of zirconium in magnesium (Fig. V.1).

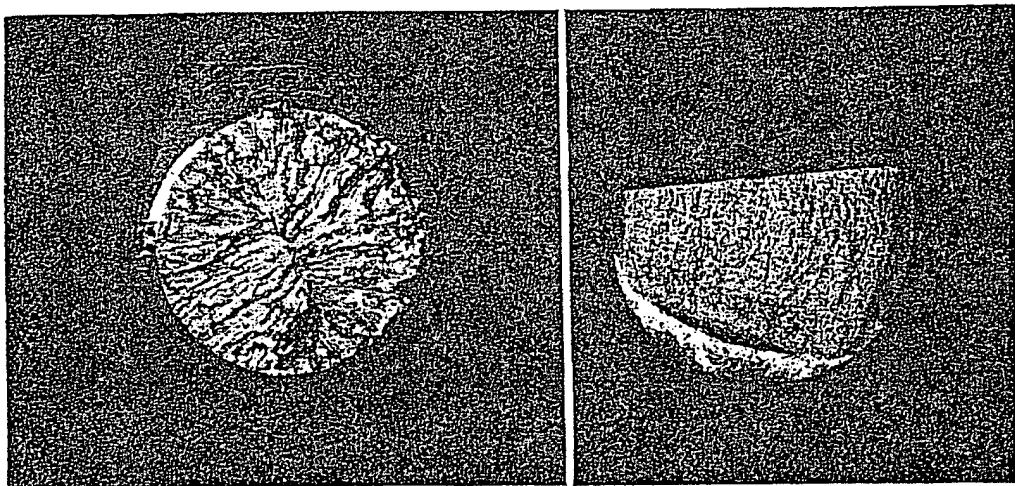


FIG. V.1. Grain refinement of magnesium by zirconium. Fractured 1 in. diameter chill cast bars in (a) pure magnesium, and (b) Mg-0.6% Zr alloy.

Sauerwald and his team, working for I.G. Farbenindustrie, rapidly surveyed methods of introducing zirconium, explored the properties of the alloys, and generally laid the foundation on which subsequent workers have built. Their original investigations were later published by Sauerwald<sup>(1-3)</sup> in a series of papers appearing shortly after the cessation of hostilities. From the early German work some intriguing facts and possibilities emerged.

(a) Only zirconium which is dissolved in the liquid magnesium at the time of pouring is effective in refining the grain of the cast metal.

(b) The maximum solubility of zirconium in liquid magnesium is about 0.6 per cent.

(c) Certain elements such as Al, Si, Sn, Ni, Fe, Co, Mn and Sb form intermetallic compounds of high melting point with zirconium. Only if

these are absent will zirconium dissolve in the magnesium and grain refinement result. Elements which are compatible with zirconium are Zn, Cd, Ce, Ag, Th, Tl, Cu, Bi, Pb and Ca.

(d) An approximate distinction between dissolved (soluble) and insoluble zirconium in an alloy can be made by dissolving a sample in dilute HCl, the zirconium in the filtrate being taken as that dissolved in the alloy.

(e) Some loss of soluble zirconium always occurs on remelting and the melts then require "revivification" with more zirconium to restore the fine grain.

(f) Although the binary Mg-Zr alloy is relatively weak, it can be stiffened up with zinc to develop very attractive proof stress values.

(g) Zirconium can be introduced into magnesium at 900°C by alloying with zirconium metal powder under argon, or at lower temperatures by salt reduction processes using various zirconium halides or complex halides.

Between appreciation of the attractive properties of magnesium-zirconium alloys and their commercial realization by MEL at reasonable cost and in a state free from flux inclusions, there was a wide gulf of effort and disappointment—leading one exasperated metallurgist to exclaim: "This zirconium business is metallurgy run mad!" Very brief outlines of some of the difficulties which were encountered have already appeared<sup>(4-6)</sup>, but no adequate account has yet been disclosed. In what follows certain aspects of the problem will be discussed, not necessarily in the order in which they were encountered. Naturally enough, formidable chemical problems arose in preparing various reducible zirconium compounds at low cost and in a state of high purity. This work, begun by S. J. Fletcher and completed by A. L. Hock and his team, lies however outside the scope of the present book. The metallurgical team at MEL, which finally developed very successful fluoride-based alloying processes, was led by the late A. C. Jessup, a remarkable man by any standard. Nevertheless without the foresight and optimism of its Chairman, Major C. J. P. Ball, it may be doubted whether this company would in fact have solved its problems.

#### *Dynamic Equilibrium in Molten Magnesium-Zirconium Alloys*

One of the most important features of Mg-Zr alloys is the nature of the equilibrium which exists in molten alloys of full zirconium content. Many factors are continually operating to precipitate zirconium from solution in molten magnesium, and it is only possible to maintain a full (soluble) zirconium content if a considerable excess of zirconium is present at the bottom of the melt in a form able to dissolve in magnesium faster than precipitation can occur. If precipitation losses of zirconium are more rapid than take-up from this zirconium "reservoir" at the bottom of the crucible, the soluble zirconium content of the melt will fall. On transfer of molten zirconium alloy into another crucible, the soluble zirconium content of the melt will at once begin to fall. Consequently all zirconium castings should be poured

**Table 1A. Chemical Compositions of Alloys**

Alloy	Al %	Mn %	Zn %	Ca %	Si %	RE %	Si %	Fe %	Ni %	Cu %	Be %	Zr %
Example1	4.8	0.26	0.15	0.25	1.35	0.08	0.01	0.003	0.0007	0.0005	0.0003	-
Example2	5.3	0.30	0.10	0.20	0.80	0.10	0.01	0.003	0.0006	0.0014	0.0004	-
Example3	6.1	0.25	0.40	0.20	0.90	0.20	0.01	0.003	0.0002	0.0012	0.0003	-
Example4	5.3	0.30	0.35	0.22	1.18	0.49	0.01	0.001	0.0005	0.0011	-	-
Example5	7.0	0.32	0.01	0.53	0.46	-	0.01	0.001	0.0008	0.0011	-	-
Example6	6.9	0.28	0.62	0.52	0.48	0.18	0.01	0.001	0.0007	0.0008	0.0004	-
Example7	7.9	0.01	0.12	0.66	0.52	0.12	0.01	0.001	0.0009	0.0011	0.01	-
Example8	7.9	0.31	0.64	0.68	0.55	0.16	0.01	0.002	0.0008	0.0016	-	-
Example9	8.8	0.24	0.11	0.85	0.51	0.03	0.01	0.001	0.0009	0.0014	-	-
Example10	8.5	0.28	0.72	0.95	0.25	0.08	0.01	0.002	0.0008	0.0017	-	-
Example11	8.7	0.07	0.15	0.85	0.15	0.24	0.01	0.001	0.0009	0.0012	-	0.01
Example12	8.9	0.18	0.48	0.65	0.05	0.75	0.01	0.002	0.0010	0.0009	0.0003	-
Example13	8.4	0.22	0.05	1.05	0.28	-	0.01	0.001	0.0008	0.0011	-	-
Example14	9.1	0.22	0.60	0.80	0.55	0.06	0.01	0.001	0.0008	0.0021	-	-
Comp Ex1	8.9	0.23	0.74	-	-	-	0.01	0.003	0.0007	0.0009	0.0009	-
Comp Ex2	4.3	0.29	0.01	-	-	2.4	0.01	0.003	0.0008	0.0008	0.0008	-
Comp Ex3	4.4	0.31	0.05	1.4	0.1	0.25	0.01	0.003	0.0006	0.0011	0.0009	-
Comp Ex4	9.4	0.19	0.54	1.3	0.45	0.05	0.01	0.002	0.0008	0.0012	0.0007	-
Comp Ex5	8.1	0.24	0.15	0.8	0.85	0.12	0.01	0.003	0.0009	0.0015	0.0004	-
Comp Ex6	5.0	0.29	0.57	1.02	0.12	-	0.02	0.003	0.0011	0.0015	0.0004	-
Comp Ex7	5.1	0.32	0.01	1.48	0.14	0.95	0.01	0.003	0.0009	0.0014	0.0004	-

**Table 3A. Die Castability Properties**

Alloy	Casting temperature [°C]	Oxidation Resistance	Fluidity	Die Sticking	Rank
Example 1	690	9.5	9	8.5	88
Example 2	690	9.5	9	9	91
Example 3	680	10	10	9.5	96
Example 4	690	9.5	9	9	92
Example 5	680	10	10	10	100
Example 6	660	10	8.5	9	91
Example 7	670	10	10	10	100
Example 8	660	10	9	9.5	95
Example 9	670	10	10	10	100
Example 10	680	10	10	9	93
Example 11	670	10	10	9.5	97
Example 12	670	10	10	9	93
Example 13	670	10	10	9.5	97
Example 14	660	10	9	9	92
Comparative Example 1	670	9.5	10	10	99
Comparative Example 2	690	8	8	9	80
Comparative Example 3	700	8	8	6	67
Comparative Example 4	670	10	10	7	80
Comparative Example 5	660	10	10	7	80
Comparative Example 6	700	9	8	6	70
Comparative Example 7	700	8	8	5	60

**Table 4A.** Mechanical Properties and Creep Behavior

Alloy	TYS [MPa]		UTS [MPa]		E%		CYS [MPa]		MCR . 10 <sup>9</sup> [S <sup>-1</sup> ]		CR mg/cm <sup>2</sup> /day
	20°C	150°C	20°C	20°C	20°C	150°C	85 MPa	150°C	85 MPa	50 MPa	
Example 1	145	112	250	10	144	112	1.8	1.8	1.1	1.48	
Example 2	145	108	244	10	147	105	1.9	1.9	1.2	1.45	
Example 3	153	116	249	9	152	118	13.6	13.6	3.2	1.40	
Example 4	153	130	253	8	155	132	1.4	1.4	1.1	0.86	
Example 5	166	135	275	10	167	130	4.8	4.8	1.1	1.24	
Example 6	164	125	272	8	165	125	5.9	5.9	1.8	1.27	
Example 7	172	140	275	8	171	138	7.1	7.1	1.5	1.01	
Example 8	175	130	272	6	174	130	8.6	8.6	2.2	1.12	
Example 9	178	142	262	5	178	140	6.9	6.9	1.8	0.93	
Example 10	175	120	260	5	174	122	11.8	11.8	2.7	1.21	
Example 11	174	121	259	5	174	122	9.4	9.4	2.5	0.98	
Example 12	164	115	252	6	166	112	12.1	12.1	2.9	1.08	
Example 13	178	135	260	4	177	122	7.2	7.2	1.9	0.95	
Example 14	182	122	266	4	181	138	11.5	11.5	2.5	1.03	
Comparative Example 1	160	105	260	6	160	105	305	305	61	1.31	
Comparative Example 2	135	100	240	12	135	100	12.4	12.4	2.2	1.62	
Comparative Example 3	143	108	235	8	142	108	7.8	7.8	2.2	1.56	
Comparative Example 4	182	138	238	1	181	137	12.2	12.2	2.3	1.41	
Comparative Example 5	180	141	232	1	179	142	8.3	8.3	2.1	1.43	
Comparative Example 6	142	107	238	6	144	108	9.4	9.4	2.9	1.67	
Comparative Example 7	144	109	232	5	143	107	7.5	7.5	2.7	1.89	